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Domains of SB Diblock Copolymers

by

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of SB Diblock Copolymers

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Abstract

Blends of perdeuterated polybutadiene homopolymer and a polystyrene-polybutadiene diblock copolymer were prepared by solution casting techniques. Small angle neutron scattering and transmission electron microscopy experiments on blends containing homopolymer with chain length smaller than the corresponding block sequence showed that homopolymer chains are solubilized by the spherical microdomains up to a homopolymer content of about 15 mole percent. The solubilized homopolymer is distributed in a spatially uniform manner throughout the domain volume and the homopolymer radius of gyration is only slightly larger than that of an unperturbed chain in bulk. At about 18 mole percent, pools of homopolymer appear outside the microdomains; the change in scattering intensities indicate that pool formation is a kinetic phenomenon rather than a thermodynamically controlled event. Experiments on blends containing longer homopolymer chains revealed a lower concentration, between 3 and 6 mole percent, for the onset of homopolymer pool formation.

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Introduction

Considerable attention has been given to the phenomenon of solubilization of homopolymers into the domains of block copolymers, including extensive experimental work (1-5) and theoretical studies (6-9). The emulsifying action of block copolymers, their influence on interfacial tension and the strong molecular weight dependence of the locations of boundaries of block copolymer/homopolymer phase diagrams are phenomena which are now well-known. Little information exists, however, on the details of the spatial organization of the solubilized homopolymers inside the block copolymer domains, although some understanding has emerged regarding the influence of solubilized homopolymer on domain size, particularly for the case of lamellar domains (2,10). The principles of small angle neutron scattering (SANS) experiments utilizing phase-matched or contrast-matched block copolymer systems (11) are well documented; a certain amount of success has been achieved in this manner in understanding the molecular-level picture for B block sequences of SB diblock copolymers (12,13,14), S homopolymers added to SB diblocks (5), B homopolymers in SBS triblocks (4) and for the spatial distribution of chain ends in spherical B domains of SB diblocks (15).

In this paper we address the specific topic of polybutadiene homopolymers inside spherical polybutadiene domains of a polystyrene-polybutadiene diblock copolymer. While the spherical geometry presents certain advantages in that isotropic scattering patterns are observed, any details of possible chain dimension pertubations in specific directions within the domain space are necessarily lost, a point emphasized recently by Hasegawa et al (14) in a study of B block chains in a lamellar morphology. Thus, although some attention is paid here to homopolymer coil dimensions inside the B microspheres, the main thrust of this work is an examination of the way in which the homopolymer chains distribute themselves throughout the domain volume. We also enquire into the phenomenon of macroscopic separation of the homopolymer at higher volume fractions and/or molecular weights to determine whether it is governed by the kinetics of our specimen preparation procedures or by thermodynamic considerations.

Experimental

Two perdeuterated Bd homopolymers and one SB diblock copolymer were prepared in our laboratory for this study. Details of the homogeneous anionic polymerization techniques, sample purification and recovery methods, and molecular characterization experiments appear in earlier publicatons from this laboratory (e.g. 5, 12, 13,15 and references therein) and are thoroughly documented in (16). Table 1 summarizes the important characteristics of the polymers employed in this work.

Specimens for SANS experiments were cast from 5 wt. percent solutions in methyl ethyl ketone using a spin casting technique described in detail elsewhere (16, 17). The temperature profile of the casting procedure was 60°C for the first 24 hours and 75°C for the following 10 hours. A continuous flow rate of 0.1 to 0.2 standard ft^3/hr of nitrogen gas was maintained through the casting cup throughout the operation.

The 0.3 mm films obtianed from the spin casting procedure were cut into 1.5 cm square pieces which were dried under vacuum with a temperature program starting at room temperature and progressing at 20-30C per day up to 120°C. Pieces were then stacked and fused together in vacuum at 120°C under slight compression (16) to produce final specimens of about 2 mm thickness for SANS experiments. Prior to SANS experiments all specimens received a final overnight annealing in vacuum at 120°C, followed by slow cooling at about 10°C/hr to room temperature. Table 2 summarizes the characteristics of the specimens examined in this investigation.

SANS experiments were carried out at the spectrometer at the National Bureau of Standards. Details of the conditions employed in the experiments and of the calibration procedures have been presented in previous publications (14-16). Transmission election microscopy of ultra-thin sections (16) of suitably stained specimens was performed on a Phillips 300 Transmission Electron Microscope operating at 80 kV and calibrated against a grating with 54,864 lines per inch.

Results

All samples listed in Table 2 were transparent in simple visual observations except for blend B2-6 which was opaque. Transmission electron microscopy revealed no evidence of "pools" of macroscopically phase-separated polybutadiene

homopolymer for samples B1-3 through B1-15 and for B2-3; three samples, B1-18, B1-20 and B2-6, did show clear evidence of polybutadiene rejected from the B domains into separate pools of homopolymer. The montage of micrographs shown in Figure 1 provides representative views taken from a large body of TEM observations.

Figure 2 shows the SANS patterns obtained for the diblock SB and for three blends B1-3, B1-6, B1-12. The observed peak near $Q = 0.022$ ($Q = 4\pi \sin\theta/\lambda$) remains essentially fixed in location while the magnitude of the peak decreases dramatically as the amount of deuteration in the spherical domains increases from 0 to 12%. When the Bd1 content is increased further so that the B domains contain 15% deuterium labelled repeat units, the maximum in the scattering pattern in essentially completely lost and a monotonically decreasing curve is observed (Figure 3). Still further increase in the content of Bd1 results in re-emergence of the maximum in the scattering pattern as shown in Figure 3; however the location of peak is now shifted to lower Q values, residing near $Q = 0.017$.

Figure 4 presents the results of SANS experiments on blends B2-3 and B2-6 which contain the higher molecular weight Bd hmopolymer. For the two low concentrations examined, the peak location ($Q = 0.022$) remains essentially constant and the peak intensity decreases as Bd2 homopolymer is added to the B domains.

Discussion

Unequivocal evidence for the appearance of pools of homopolymer rejected from the block copolymer domain structure is provided by the electron microscopy. In the series of blends containing the lower molecular weight polybutadiene homopolymer (Bd1, $M=8,900$g/mole), samples B1-18 and B1-20 contained numerous blobs of polybutadiene homopolymer with a characteristic size of about 700 Å; in the series containing Bd2 ($M=23,700$g/mole), sample B2-6 contained similar pools of homopolymer. While this evidence supports the general picture of enhanced homopolymer rejection from the block copolymer morphology at higher homopolymer molecular weights and/or homopolymer weight fractions, the TEM experiments alone cannot clarify whether or not the block copolymer domains are fully saturated with homopolymer when the blobs of rejected homopolymer first appear in the morphology. The resolution of this issue would determine whether the solvent spin-casting procedure used to prepare the blends in this work produces block

copolymer/homopolymer blends which are close to equilibrium or blends which present a kinetically controlled, process dependent morphology.

To answer this question we turn to the SANS data of Figures 2-4. In Figure 2, the SANS intensity decreases continuously through the series of samples SB to B12 indicating that the added perdeuterated polybutadiene is uniformly filling the neutron scattering contrast sink which the polybutadiene spheres represent relative to the polystyrene matrix. When the deuterium content of the polybutadiene domains is about 15% in sample B1-15, this contrast sink has essentially disappeared as evidenced by the scattering pattern for this blend (Figure 3) which contains no peaks from structural scattering. Upon further addition of Bd1 homopolymer, the scattering intensity _increases_ and the structural scattering _reappears_ (although at a significantly lower value of Q), indicating that the polybutadiene domains now represent regions of neutron scattering contrast which _exceed_ that of the polystyrene matrix. This clearly indicates that, although some of the added homopolymer is rejected into the large blobs seen in the micrographs of blends B1-18 and B1-20, a significant amount of the incremental perdeuterated homopolymer is taken up by the polybutadiene domains; thus the observed onset of homopolymer rejection around 20 weight percent in this series of blends is a kinetic phenomenon dictated by the solvent casting process. Given the opportunity to approach equilibrium, both blends B1-18 and B1-20 would exhibit a reduced amount of the homopolymer pools appearing in the micrographs; from the data available here, it is not possible to determine whether or not these would completely disappear at equilibrium.

Further evidence for the nonequilibrium nature of the homopolymer rejection process is contained in Figure 4. Here, the added homopolymer forms pools in blend B2-6 but not in B2-3. Both of these blends contain amounts of homopolymer well below the point of contrast matching so that the polybutadiene regions of both blends represent contrast sinks in the SANS experiment. The reduced SANS intensity of sample B2-6 compared to that of B2-3 indicates that, in addition to forming pools, some of the incremental homopolymer was incorporated into the spherical microdomains thereby reducing the contrast mismatch.

Inspection of Figures 2-4 also indicates that the appearance of homopolymer pools results in a significant amount of scattering at very low values if Q which does not occur in the blends which are free of the large pools. In addition, there is a shift to lower Q and a significant broadening of the main SANS peak

for samples B1-18 and B1-20; SAXS data (16) on B1-20 showed neither the broadening nor the shift in the scattering and only a small amount of excess scattering at very low Q. We attribute the observed broadening and apparent shift of the main peak to the formation of pools of polybutadiene homopolymer (See Figures 1c and 1d). Since these pools are of perdeuterated material, their inherent scattering-length density for neutrons is very much greater than that of the nearly contrast-matched spherical microdomains, while their effect on the SAXS spectrum would be minimal.

We now turn our attention to the conformation of the homopolymer chains inside the spherical polybutadiene microdomains. Following the example of Hasegawa et al (14) we have employed a Guinier-plot analysis scheme (20) to extract an effective radius of gyration for the caged homopolymer. In principle, only data for fully contrast-matched blends, for which no structural scattering is present, can be used in this type of analysis; nevertheless, Hasegawa and coworkers (14) have shown that small amounts of residual structual scattering in nearly matched compositions do not interfere with the analysis if it is carried out properly. Therefore we have chosen blends B1-12 and B1-15 for the Guinier analysis; unfortunately neither of the blends containing the higher molecular weight homopolymer was sufficiently close to contrast matching to warrant the analysis of single chain behavior.

Figure 5 shows the Guinier plots obtained for the two blends. Over a considerable range of the data shown, the Guinier approximation,

$$I(q) \sim \exp(-Q^2 R_g^2) \qquad (1)$$

holds reasonably well, where Rg is the radius of gyration of the perdeuterated homopolymer chain inside the spherical domains. At low Q, deviations from Equation 1 are observed owing to the residual structural scattering and at high Q the data trail off above the Guinier fit as expected (14) whenever the product QRg becomes larger than about 1.3. From the slopes we obtain Rg values of about 36 Å for homopolymer Bd1 in blend B1-12 and 39 Å for Bd1 in blend B1-15. This may be compared with the value of about 35 Å expected from an unperturbed Gaussian coil of perdeuterated polybutadiene of molecular weight 8,900g/mole (12,16). Thus, even though there are various uncertainties in this analysis, it is reasonable to conclude that the homopolymer chains inside the spherical domains adopt relatively unperturbed configurations.

Finally, we have examined the reduction in the SANS contrast factor which occurs with homopolymer addition, following procedures identical to those recently reported (15,16). Figure 6 is a plot of normalized intensity I_N (integrated intensity of a given sample from Q=0.012 to 0.032 divided by the integrated intensity of SB over the same range) versus the mole fraction of deuterium in the polybutadiene domains. The solid curve is based on Koberstein's equation for the contrast factor (4,11) for block copolymer/homopolymer mixtures using densities of 1.05 for polystyrene and 0.895 for polybutadiene. The data points shown in Figure 4 are for those samples for which no pools of rejected polybutadiene homopolymer were observed, i.e. samples in which all of the added homopolymer entered the spherical domains. As shown in Figure 6, the normalized intensities for these samples decrease according to the predictions of Koberstein's contrast factor expression. Because this expression is based on the assumption of a spatially uniform distribution of deuterium-labelled species, it appears that the added homopolymer is essentially uniformly distributed within the volume of the spherical domains over the concentration range of the data in Figure 6. While pooling of the homopolymer at the domain centers evidently does not occur for any of the blends represented in Figure 6, there is no evidence in our data to reject this possibility for blends containing larger amounts of added homopolymer.

Conclusions

Relatively short (M homopolymer< M block sequence) homopolymer chains of perdeuterated polybutadiene are completely solubilized by the spherical microdomains of an SB diblock copolymer up to the point at which about 15 mole percent of the repeat units in the domains come from the homopolymer. The solubilized homopolymer is spread essentially uniformly throughout the domain volume and the homopolymer radius of gyration is only very slightly larger than that of an unperturbed homopolymer of the same molecular weight. At about 18 mole percent of this same homopolymer, pools of homopolymer form outside the B microdomains; the rejection of homopolymer observed at this concentration is a kinetic phenomenon reflecting the conditions employed in the solution casting procedures used to form the blends. Thus, comparisions between the observed onset of homopolymer rejection from the block copolymer mesophase and the predictions of theories (e.g. 6,7) of this phenomenon must be done with caution;

perhaps only qualitative comparisons are warranted.

Longer homopolymer chains (M homopolymer>M block sequence) behave in a similar manner except that the observed kinetically controlled solubility limit is lower, lying somewhere between about 3 and 6 mole percent.

<u>Table 1</u>   <u>Molecular characterization polymers</u>

<u>Polymer</u>	<u>Molecular Weight</u>[a]	<u>Polybutadiene microstructure</u>[b]
SB	S=90,000; B=11,000	-/-/10
Bd1	8,900	44/51/5
Bd2	23,700	44/51/5

(a) g/mole; Mw/Mn< 1.1

(b) cis 1,4/trans 1,4/vinyl from proton and carbon 13 NMR (16)

Table 2   Samples examined in SANS experiments

Sample code	Wt % homopolymer Bd in B domains [a]	Mole % deuteration of B domains [b]	Volume % Polybutadiene domains in sample [c]
SB	0	0	13
B1-3	3.5	3.1	13
B1-6	6.8	6.1	13
B1-12	14	12	14
B1-15	17	15	14
B1-18	20	18	15
B1-20	23	20	15
B2-3	3.5	3.1	13
B2-6	7.0	6.2	13

(a) Blends with B1-X code contain perdeuterated homopolymer Bd1(M=8,900g/mole); B2-X blends contain Bd2(M=23,700g/mole).

(b) Accounts for the difference in repeat unit molecular weight for B and Bd and for the 98% level of deuteration (16) in the Bd homopolymers.
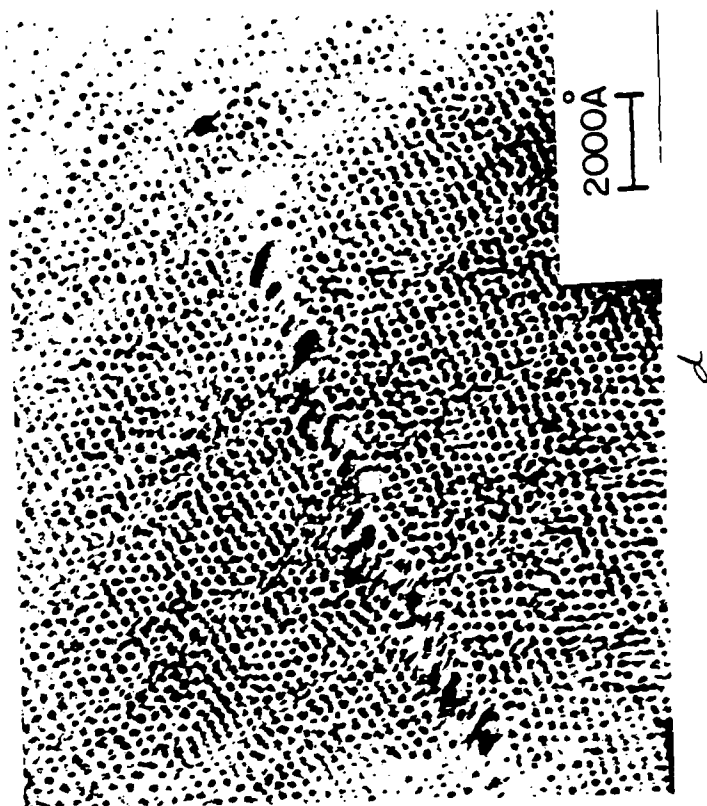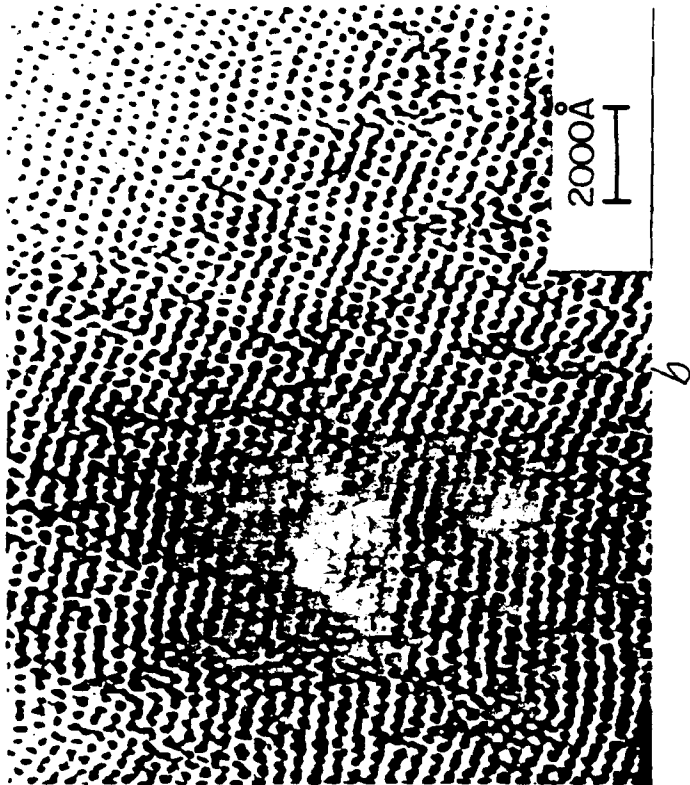
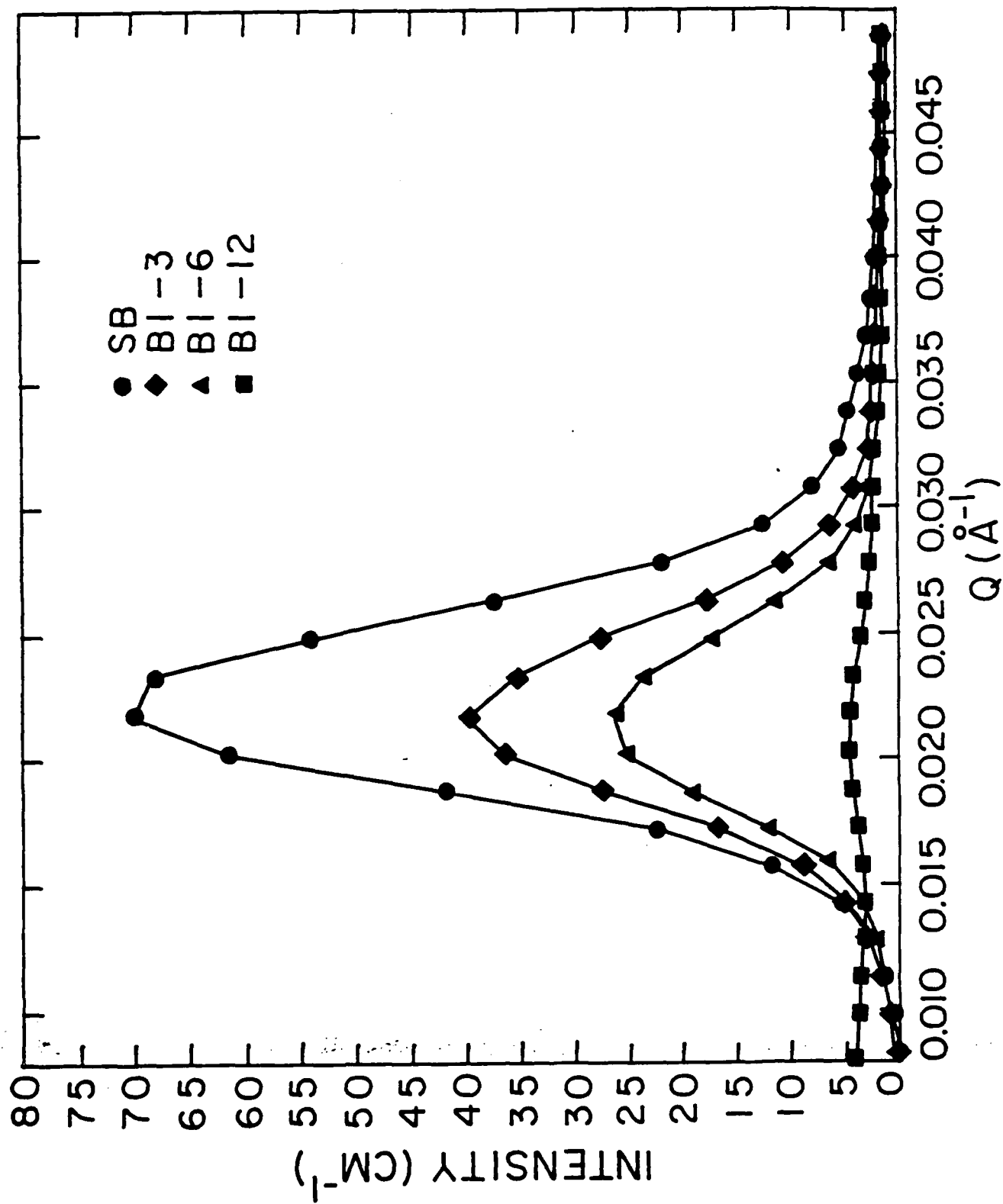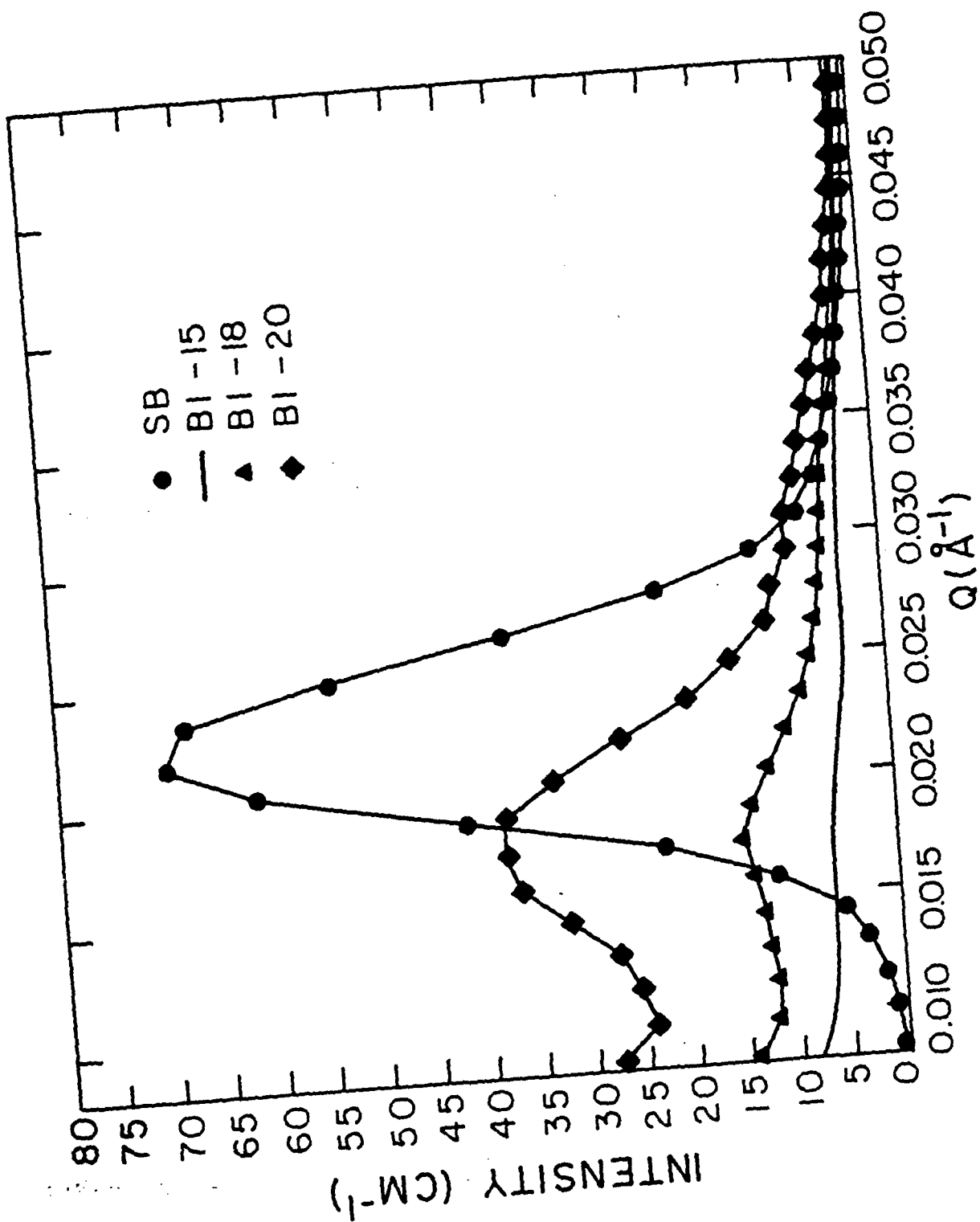(c) Based on densities of 1.05 g/cc for polystyrene and 0.895 for polybutadiene.

References

1. Reiss, G.; Kohler, J.; Tournut, C., Banderet, A. _Makromol Chem_. 1967, _58_, 101.

2. Roe, R.J.; Zin, W.C.; _Macromolecules_, 1984, _17_, 183 and 1984, _17_, 189.

3. Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. _Macromolecules_, 1970, _3_, 87.

4. Quan, X.; Gancarz, I.; Koberstein, J.T.; Wignall, G. _J.Polymer Sci._, _Polymer Physics_, 1987, _25_, 641.

5. Berney, C.V.; Cheng. P.; Cohen, R.E. _Macromolecules_, in press

6. Hong, K.M.; Noolandi, J. _Macromolecules_, 1983, _16_, 1083.

7. Whitmore, M.D.; Noolandi, J. _Macromolecules_, 1985, _18_, 2686

8. Meier, D.J. _A.C.S. Polymer Preprints_, 1977, _18(1)_, 340

9. Leibler, L.; Orland, H.; Wheeler, J.C. _J. Chem. Phys._, 1983, _79_, 3550

10. Quan, X.; Gancarz, I.; Kobertstein, J.T.; Wignall, G. _Macromolecules_, 1987, _20_, 1431.

11. Quan, X.; Koberstein, J.T. _J. Polymer Sci._, _Polymer Physics_, 1987, _25_, 1381.

12. Bates, F.S.; Berney, C.V.; Cohen, R.E.; Wignall, G. _Polymer_, 1983, _24_, 519.

13. Berney, C.V.; Kofinas, P.; Cohen, R.E. _Polymer Communications_, 1986 _27_, 330.

14. Hasegawa, H.; Hashimoto, T.; Kawai, H.; Lodge, T.; Amis, E.; Glinka, C.; Han, C. _Macromolecules_ 1985, _18_, 67.

15. Cheng. P.; Berney, C.V.; Cohen, R.E. _Macromolecules_, submitted.

16. Cheng. P., ScD Thesis, Massachusetts Institute of Technology, 1988.

17. Bates, F.S.; Cohen, R.E.; Argon, A.S., _Macromolecules_, 1983, _16_, 1108.

18. Berney, C.V.; Cohen, R.E.; Bates, F.S., _Polymer_, 1982, _23_, 1222.

19. Bates, F.S.; Cohen, R.E.; Berney, C.V.; _Macromolecules_, 1982, _15_, 589.

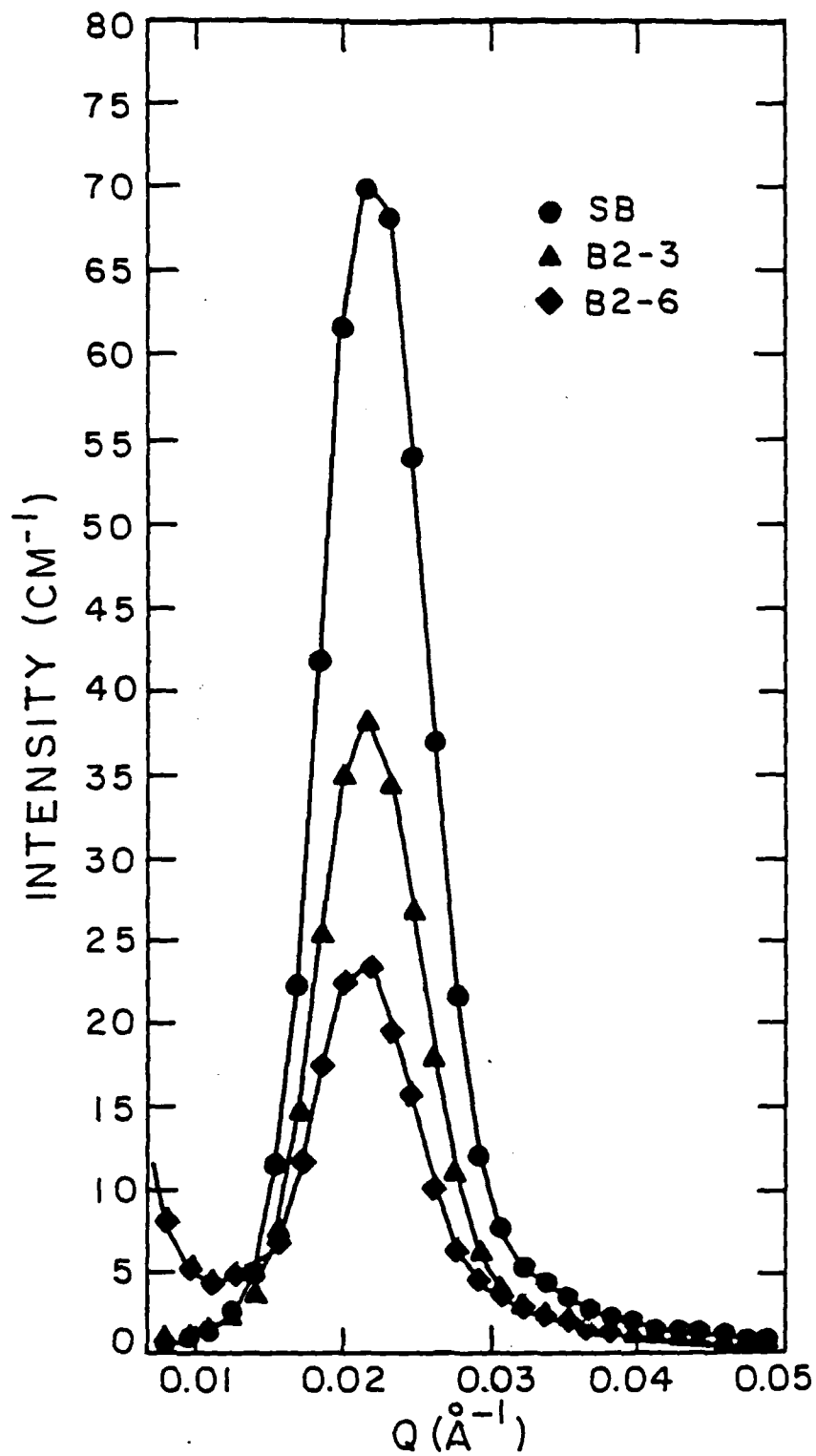20. Guinier, A.; Fournet, G.; Small Angle Scattering of X-Rays, Wiley, N.Y. 1955.
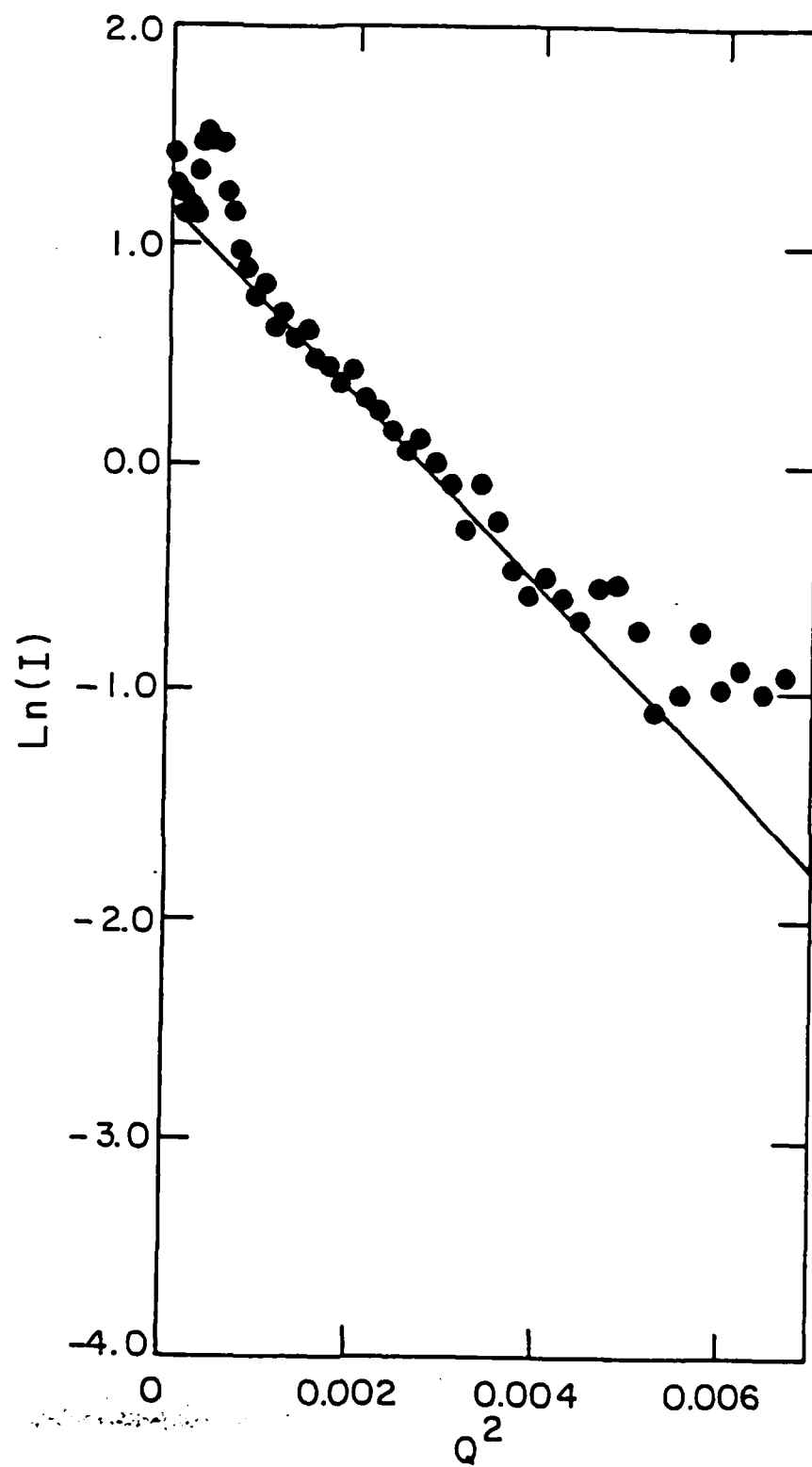
Figures

1. Transmission electron micrographs of osmium-tetroxide stained sections of: (a) Bl-3, (b) Bl-12, (c) Bl-20, (d) B2-6.

2. SANS data for SB and three blends containing homopolymer Bdl, M=8,900 g/mole.

3. SANS data for SB and three blends containing homopolymer Bdl, M=8,900 g/mole.   Blend Bl-15 is the nearly perfectly contrast-matched composition; blends Bl-18 and Bl-20 contains pools of homopolymer rejected from the microphase separated morphology of the block copolymer.

4. SANS data for SB and two blends containing Bd2, M=23,700g/mole.

5. Guinier plots for: (a) Bl-12 and (b) Bl-15.

6. SANS intensity as a function of mole fraction of perdeuterated repeat units within the polybutadiene spheres assuming uniform distribution of the perdeuturated material.   Solid line: expected behavior based on references (4) and (11). Data points for samples indicated, normalized to SB intensity.
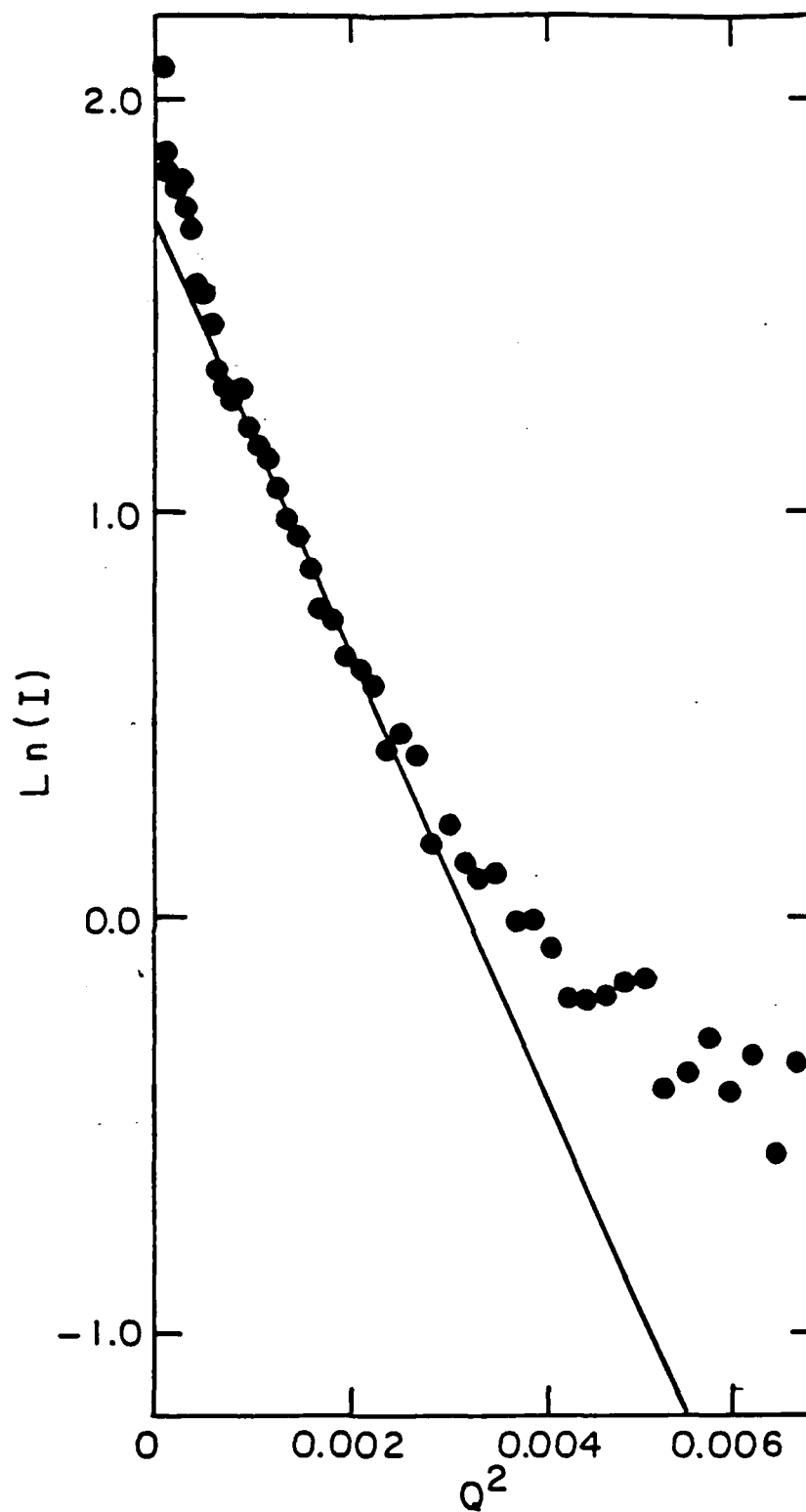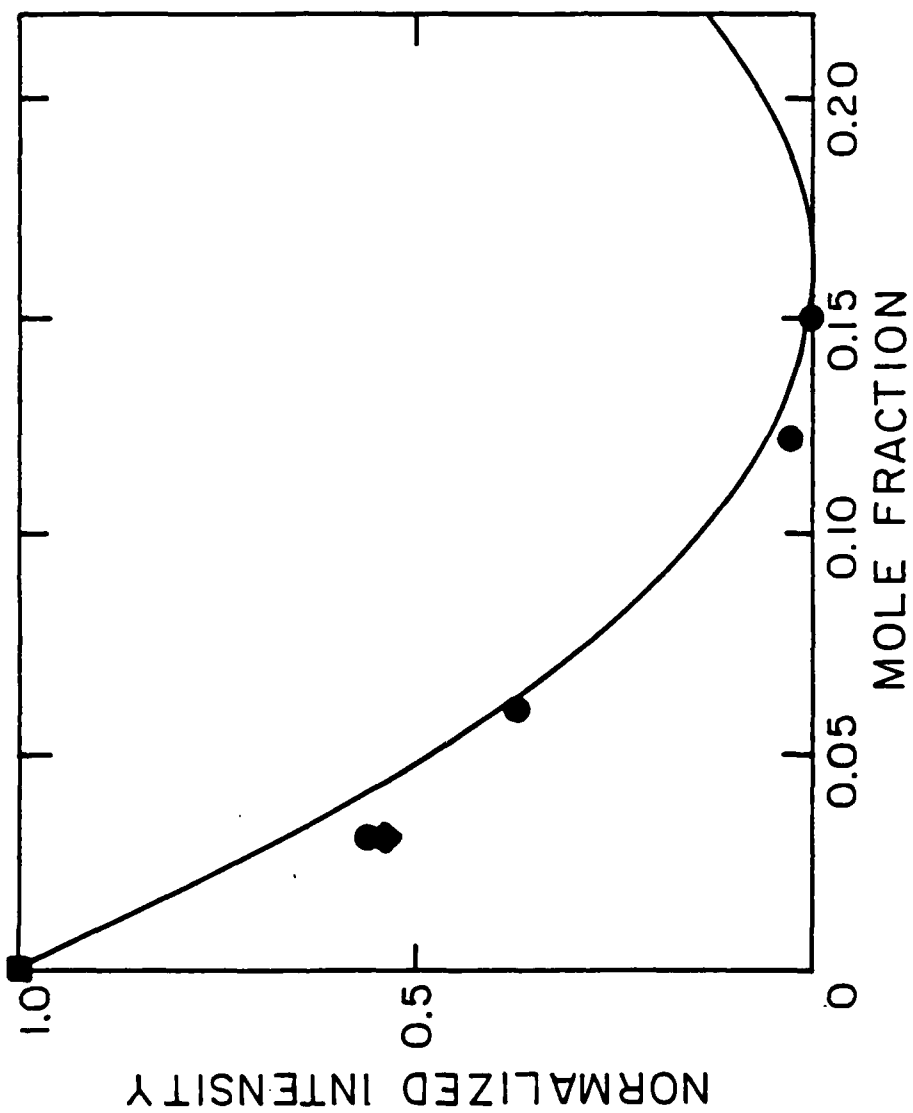
a

b

c

d

1000 Å

2000Å

5000 Å

2000Å

Legend:
- ● SB
- — BI-15
- ▲ BI-18
- ◆ BI-20

X-axis: Q (Å⁻¹)
Y-axis: INTENSITY (CM⁻¹)

5a

5b
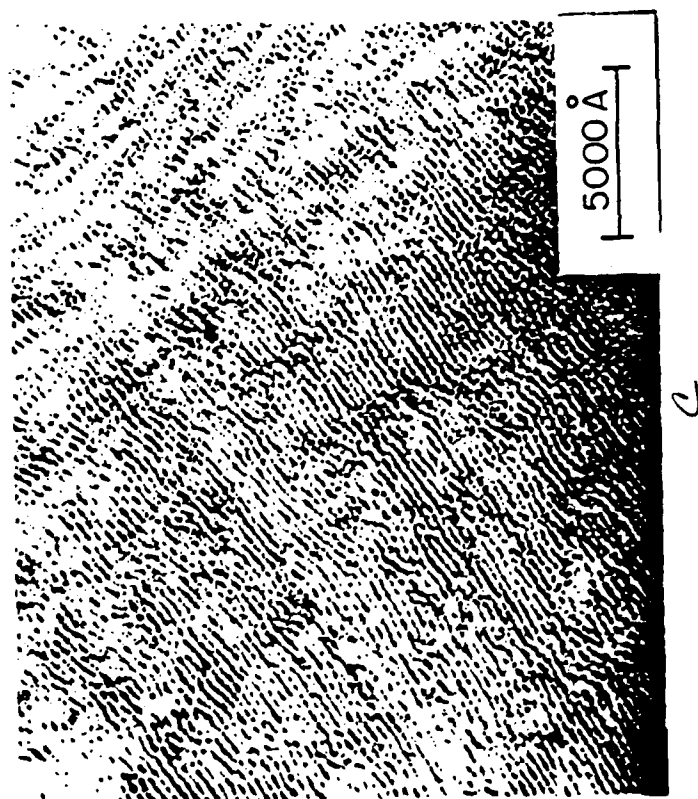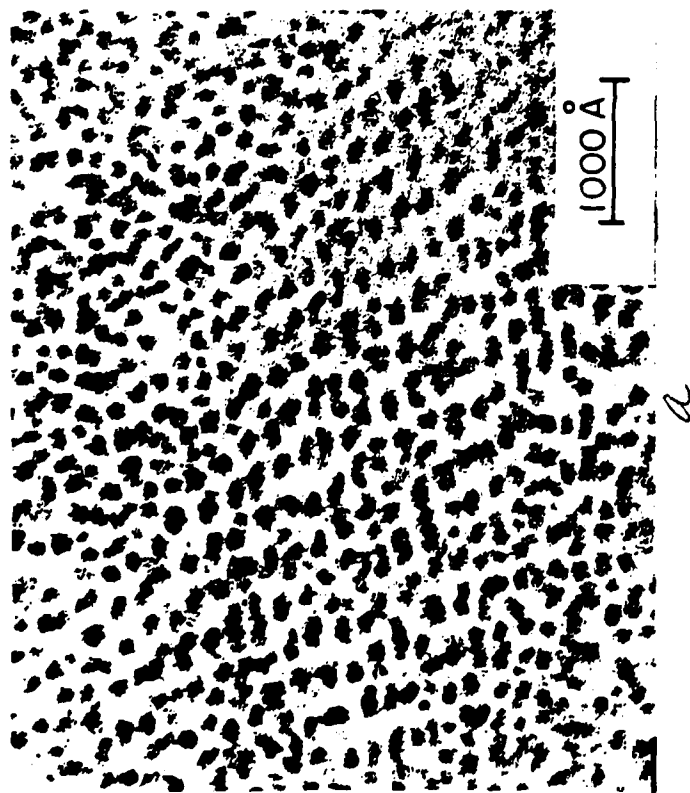
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